reducing atmosphere where a barium aluminum potassium silicate results containing about 36 per cent silica. This is run into water while molten and the granulated material ground and floated. The settled material is then treated as a paste with the proper quantity of sulfuric acid which decomposes it perfectly, giving a solution of alum and aluminum sulfate and a solid residue consisting of nearly equal parts of very finely divided barium sulfate and silica. It might be supposed that the silica would be so gelatinous as to be unwashable, but this has not been found true. On the contrary, where properly manipulated, the precipitate is somewhat granular, but entirely free from grit, and forms an excellent material, after ignition, for use as a pigment in printing ink, rubber incorporation and as a coating for paper. In value we believe this material will be found to be superior to very pure china clay. As you will see[1] from the sample submitted, it has a beautiful white color.

The solution, when evaporated, yields the potash as potash alum, and if the little iron present be kept in the ferrous condition, this alum, after washing with a little water and whizzing, is entirely free from iron and well suited for the preparation of pure potassium sulfate and iron-free alumina or aluminum sulfate, as desired. We expect to sell our alum as such so far as the market will take it and decompose only so much of it as may be necessary. This process may, therefore, furnish no potash at all. But inasmuch as potash for alum production now comes from over seas, this method is an indirect contribution to the supply.

The solution never contains enough potash to precipitate all the aluminum as alum. An excess of aluminum sulfate remains in the mother liquor together with the sodium and a little iron. This is allowed to cool and is broken up, furnishing a material equal in value to that now made from bauxite.

LAFAYETTE COLLEGE, EASTON, PA.

AVAILABILITY OF ORGANIC NITROGEN[2]

By J. E. BRECKENRIDGE

Received April 12, 1915

In the last few years this subject has been coming to the front very rapidly. In some of the northern states more unscrupulous manufacturers secured all their nitrogen in their 1 per cent nitrogen brands from garbage tankage and peat. The state control officials soon became aware of the practice and argued that the farmer was paying for first-quality readily active nitrogen and received an inert and less expensive nitrogen; in other words, the farmer was not receiving full value for his money. This fact led to a thorough investigation as to the methods by which the control people could identify the activity of organic nitrogen. Much criticism was made as to the rendering available of inert organic nitrogen such as horns, hoofs, hair, leather, feathers, fur waste, etc., by digesting in sulfuric acid. While it was believed possible, it was considered that manufacturers were not doing it.

This led to the appointing of a committee to arrange, if possible, for a visit to some factory to watch the process. Such arrangements were made. Samples of all materials which went into the mixing were drawn as they entered the mixer. One hundred and fifty tons were mixed, the den sealed by officials and allowed to stand 48 hours. Then the seal was broken, and in the presence of the state committee, the den was discharged and samples drawn. This sample was used to further investigate the methods for active organic nitrogen.

From this investigation came the publication of a pamphlet dated March 4, 1911, entitled "A Method for Examining the Activity of Organic Forms of Nitrogen," signed by the directors of the New York, New Jersey, and New England States Experiment Stations.

This pamphlet included instructions for carrying out the Alkaline Permanganate Method and results obtained by seven Experiment Stations' Laboratories on the three samples.

SAMPLE NO. 1 was base goods made from hair waste, treated sole leather, garbage tankage and sulfuric acid. The average test on this was:

	Per cent		Per cent
Total nitrogen	1.75	Water-soluble organic	1.01
Nitrogen as ammonium salts	0.25	Water-insoluble organic	0.49
Total organic	1.50	Active insoluble	0.21
		Inactive insoluble	0.28

The percentage availability of the insoluble by this method on this sample varied from 39.21 to 47.36 per cent, a difference of 8.15 per cent.

SAMPLE NO. 2 was made from blood (100 parts), cottonseed-meal (50 parts), acid phosphate (500 parts) and muriate of potash (75 parts). Average total nitrogen, 2.50 per cent. The percentage of available insoluble nitrogen varied from 61.11 to 77.97 per cent.

SAMPLE NO. 3 was made from treated sole leather (200 parts), garbage tankage (150 parts), peat (100 parts), acid phosphate (500 parts), and muriate of potash (50 parts). The average total nitrogen was 2.09 per cent. The percentage availability of insoluble nitrogen varied from 37.06 to 53.03 per cent.

The following forms for expressing results were suggested:

LONG FORM, to be used where nitrates and ammonia are present and determined:

Nitrogen as nitrates
Nitrogen as ammonium salts
Water-soluble organic nitrogen
Active insoluble organic
Inactive insoluble organic
Total nitrogen

SHORT FORM (where it is desired to shorten the above procedure):

Water-soluble nitrogen
Active insoluble organic
Inactive insoluble organic
Total nitrogen

We also have in this pamphlet a chart showing the comparison as to availability of insoluble nitrogen, of the results by the Alkaline Method and pot experiments.

This was the first instance of grading of quality of organic nitrogen by chemical methods. Jones of the Vermont Station had done much work on this and was the first to report this kind of work; he reported according to the long form, giving the water-soluble organic nitrogen, as well as the nitrates, ammoniacal,

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[1] Samples of all materials were furnished for inspection.

[2] Chairman's Address, Fertilizer Division, 51st Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.

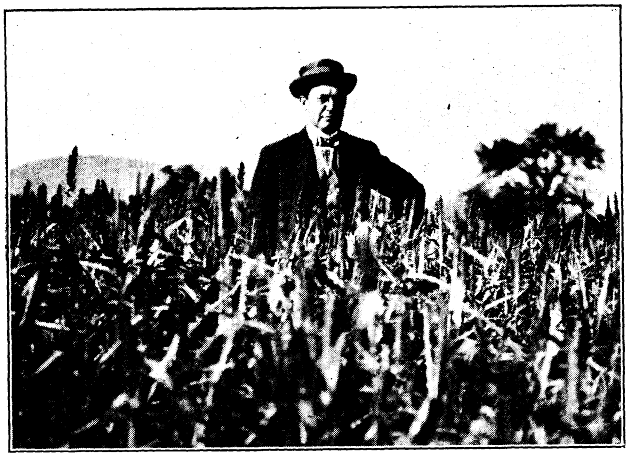

FIG. I—BLANK—NO FERTILIZER

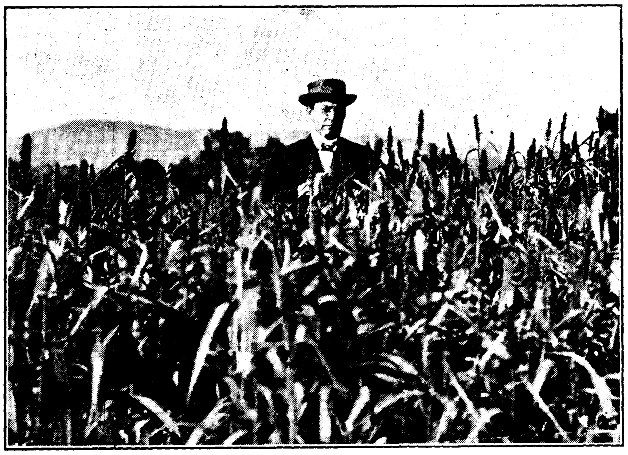

FIG. II—NITROGEN AS SODIUM NITRATE

and insoluble nitrogen. His classification of the quality of the organic nitrogen was based on the water-soluble organic, plus the active insoluble, a reasonable and perfectly just and fair basis for classification.

Street, of Connecticut, carried on further experiments with the Neutral Permanganate Method and found that mixtures of acid phosphate and so-called high-grade ammoniates such as blood and tankage caused the neutral method to give lower results in such mixtures than in the materials themselves. On suggestion of the writer, sodium carbonate was added to the neutral permanganate solution just before adding the material to be analyzed, and the results on mixtures of acid phosphate and high-grade ammoniates were much more satisfactory. From this work came the so-called Modified Neutral Permanganate Method.

Both the Alkaline and Modified Neutral have been tried out by the A. O. A. C. and have been adopted, the Alkaline being adopted by the northern and middle western states and the Neutral being preferred by the southern states. Other methods have been suggested for determining the availability of organic nitrogen, such as "A Bacteriological Method for Determining Availability of Organic Nitrogen" by McCandless and Atkinson"[1] and "Bacteriological Method for Determining the Availability of Nitrogen in Fertilizers" by Dr. Lipman.[2] Neither of these methods have had any wide application because the Alkaline and Modified Neutral were much simpler and easier to manipulate.

From Vermont the use of the Alkaline Method has spread to Massachusetts, Maine, Rhode Island, New Jersey, Pennsylvania, Michigan and Indiana, with the probability of other states doing this line of work.

The Fertilizer Industry welcomes anything that will drive the unscrupulous manufacturers from the business, but does not welcome anything that causes unjust discriminations.

The interpretation of the results from any of these methods must be with a view to give justice to all classes of ammoniates. During the first of this work credit was given to the water-soluble organic nitrogen and the availability of the organic nitrogen was considered to be the water-soluble organic plus the active insoluble, which was a reasonable, just and fair ruling.

As an illustration of this, I quote the experiments of Hartwell and Pember[1] "average relative increase in yield (blood at 80 per cent) Base Goods nitrogen 84 per cent." This was on pot experiments where all the nitrogen of base was used. Another result was on the soluble part of Base, page 443 of above article—"soluble part of Base seems to have had an availability higher than blood, the insoluble part useless."

Taken as a whole, we have a material in the wet mixed base goods testing total nitrogen 1.68 per cent, soluble nitrogen 1.28 per cent, and insoluble nitrogen 0.40 per cent, which is rated by the above pot experiments as 84 per cent of the nitrogen available, but if rated on the insoluble portion, it is useless. The consumer in buying this quality of nitrogen is getting as much, if not more, for his money than he would if he bought blood nitrogen.

Again some pot experiments were carried out on millet and the accompanying cuts illustrate well the value of base goods nitrogen in comparison with no fertilizer, cottonseed meal and nitrate of soda, the amounts of fertilizer used representing the same amount of nitrogen ($1^1/_4$ lbs. per $^1/_{20}$ acre) in each case.

This subject is not one to be considered lightly whether or not it is believed that the methods employed are accurate. The facts are, these methods are being used and the fertilizer manufacturers should live up to these requirements as specified by the various states.

We have as the latest comments on this subject, the following:[2] "the use of low-grade and, therefore, cheap nitrogen supplies whose nitrogen by chemical treatment has been made useful for plant food, is laudable, provided the materials are sold for what they are, instead of being sold at the prices of nitrogen in high-grade nitrogenous ingredients."

According to this, the manufacturer is given no credit for gathering waste products and spending time and money in perfecting process and machinery which will handle such materials, but should sell such nitrogen at a cheap price because the crude materials from which he has obtained his nitrogen are cheaper than so-called high-grade nitrogen. It would be as reasonable to

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[1] THIS JOURNAL, **3**, 174.

[2] *Ibid.*, **2**, 146.

[1] THIS JOURNAL, **4**, 442.

[2] Pennsylvania Bulletin No. 259, page 20.

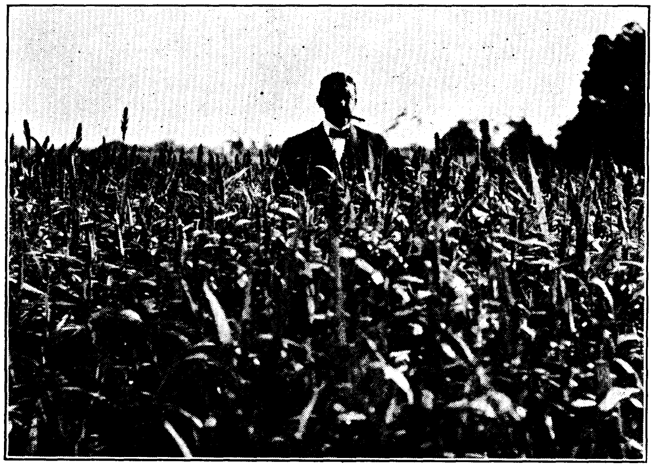

FIG. III—NITROGEN AS COTTONSEED MEAL

say that sulfate of ammonia should be sold cheaper than so-called high-grade nitrogen, because it comes from coal and that is cheap.

I believe the Fertilizer Industry has been, and is willing, to coöperate along any lines which will promote progress, and it seems to me that the Fertilizer Division of the American Chemical Society has a work along the line of availability of nitrogen which is well worth serious thought.

CARTERET, NEW JERSEY

THE DESTRUCTIVE DISTILLATION OF PACIFIC COAST KELPS

By D. R. HOAGLAND

Received April 6, 1915

The giant kelps of the Pacific Coast have received considerable attention in recent years, because of their high content of potash and iodine. The production of these substances from kelp on a commercial scale was first suggested by Balch[1] and the studies were later continued by the Bureau of Soils.[2] A more extended chemical investigation, however, seemed essential, and was undertaken by this laboratory. The principal results and conclusions of this work are reported elsewhere.[3]

In order to increase the margin of profit in the kelp industry, attempts have been made to find some method of utilizing the organic matter in addition to the potash and iodine. Among the suggestions, destructive distillation was considered. It is the purpose of this paper to report experiments dealing with this particular phase of our investigations.

Balch compared the distillation of kelp with that of beech wood and states that the volatile products from kelp—acetic acid, methyl alcohol and tar—"may be regarded as approximating in value those of beech wood." He assumes a value of $6.00 per ton of dry material for the volatile products of distillation. Green and Johnson[4] afterward made two distillations of 3-lb. samples of nereocystis and expressed the opinion that the distillates were worthless, but no analyses or details were given. Turrentine[1] distilled a 3-kg. sample of *Macrocystis pyrifera* in a Hornsy rotary still. An analysis of the gas evolved is given, but no data regarding the distillates. Further experimentation seemed necessary in order to make a more definite valuation of the volatile products.

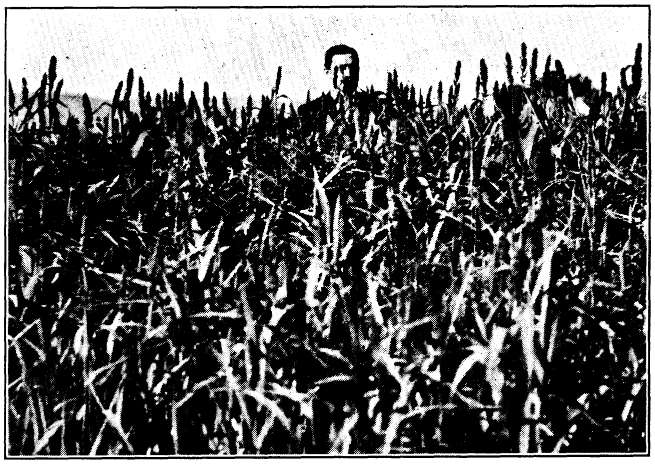

FIG. IV—NITROGEN AS BASE GOODS

The distillations in this laboratory were conducted in an iron retort of about 1.5 gallons capacity. This was provided with a pyrometer and a suitable condenser. It is realized that distillation experiments on a small scale are not comparable with commercial practice, except to a limited extent. As a control, therefore, samples of oak and Douglas fir were distilled under identical conditions. It was hoped in this way to obtain a fair idea of the comparative value of the kelp. We believe such a comparison is permissible, especially since the yields of acid and alcohol for the oak and Douglas fir approximate those obtained in larger experiments on similar materials.[2] The methods of analysis were similar to those described by the U. S. Forest Products Laboratory.[3] The acetic acid was distilled with steam from a phosphoric acid solution.

Table I shows that the average yield of acetic acid was scarcely 0.2 that of Douglas fir and only 0.1 that of oak. The alcohol yields were in the same proportions. Tar oils to the extent of 4 to 7 per cent of the dry weight of the kelp separated out in the distillate. Most of the tarry material floats on the watery distillate. The tar oil analyzed as follows:

Sp. gr. at 17° C.	DISTILLATION FRACTIONS—PERCENTAGES 0 to 125° C.	125 to 250° C.	250 to 300° C.	Tar residue
0.984	11	27	23	39

The residue solidified to a hard, black, lustrous mass.

The kelp distillates were very slightly acid to litmus, but contained considerable amounts of basic substances. By the Kjeldahl method 3.2 g. of nitrogen were found in the total distillate from 1 kg. of dried kelp, approximately $^1/_4$ to $^1/_5$ of the total nitrogen contained in the material. It does not appear that ammonium compounds could be recovered from the liquors in commercially important quantities.

The gases evolved were not combustible during any of the early stages of the distillation, differing therein

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[1] Balch, THIS JOURNAL, **1** (1909), 777.

[2] U. S. Senate Document, No. **190**.

[3] Burd-Calif. Exp. Station, *Bull.* **248**, and manuscripts in press by D. R. Hoagland and G. R. Stewart.

[4] Green and Johnson, *Chem. Eng.*, **15** (1912), 55.

[1] Turrentine, *Proc. Eighth Internat. Cong. Applied Chem.*, **15**, 313.

[2] Hawley and Palmer, *Proc. Eighth Internat. Cong. Applied Chem.*, **6**, 138; Benson, *Ibid.*, **25**, 331.

[3] Hawley and Palmer, *loc. cit.*